1.0

1.1

1.25

4.5
5.0
5.6

2.8

3.2

3.6

4.0

1.4

2.5

2.2

2.0

1.8

1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Definition of Chemical and Electrochemical Properties of a Fuel Cell Electrolyte		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report. March 25, 1977–December 24, 1977
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Sarada, T., McIntyre, John F., and Foley, R.T.		8. CONTRACT OR GRANT NUMBER(s) DAAK70-77-C-0080
9. PERFORMING ORGANIZATION NAME AND ADDRESS The American University Washington, D.C. 20016		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1T161102A34A 03 100 EF
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Mobility Equipment Research and Development Command, Fort Belvoir, Virginia		12. REPORT DATE February 1978
		13. NUMBER OF PAGES 36 + iv
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

T. Sarada

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

John F. /McIntyre
R. T. /Foley

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Electrochemistry, Fuel cell, Electrolytes, Conductivity, Polarization

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The present research is oriented toward the task of developing an improved electrolyte for the hydrocarbon-air fuel cell. A literature study of the properties of organic acids indicated that the following typed of compounds warranted further investigation:

1. Aromatic poly carboxylic acids - partially neutralized

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2. Perfluoroaliphatic carboxylic acids

3. Mono, di and poly sulfonic acids.

4. Substituted sulfonic acids

This was followed by an experimental program wherein the vapor pressure, wetting characteristics, electrical conductivity, chemical stability, and electrochemical stability were measured.

DEFINITION OF CHEMICAL AND ELECTROCHEMICAL PROPERTIES

OF A FUEL CELL ELECTROLYTE

Interim Technical Report

by

T. Sarada, John F. McIntyre and R. T. Foley

February 1978

to

U. S. Army Mobility Equipment Research and
Development Command

Fort Belvoir, Virginia

Prepared by

The American University

Washington, D.C.

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SUMMARY

The present research is oriented toward the task of
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FOREWARD

This research on the chemical and electrochemical properties of fuel cell electrolytes has been sponsored by the U. S. Army Mobility Equipment Research and Development Command at Fort Belvoir, Virginia, under Contract No. DAAK 70-77-C-0080 with the American University. The work was authorized under DA Project/Task/Work Unit No. 1T1611 02A34A 03 100 EF.

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I. ORIENTATION OF PRESENT RESEARCH TO OVERALL FUEL CELL PROGRAM

The tremendous amount of technical work performed during the
last two decades has demonstrated that the fuel cell is indeed a
feasible energy conversion device. A recent study (1) has described
in detail the impact on the national economy of commercial applications
of fuel cell power plants. Some of the same factors that bear on the
employment of fuel cells by electric utilities also are pertinent to
U.S. Army applications of fuel cells to vehicle propulsion and auxiliary
power units. These include fuel conservation leading to energy cost
savings, as well as better control of noise and emission levels.
Further, fuel cells are more amenable to sizing to meet load requirements.
For example, unlike some of the other methods of energy conversion,
fuel cell capacity need not be installed at the ultimate required
load level but rather, can be added in steps. The employment of
modules to meet gradually increased demands is described in the report
cited above (1). It is generally accepted now that the fuel cell
offers distinct advantages for energy conversion plants of any size.

While the research and development in the fuel cell field
has demonstrated the feasibility of the fuel cell as an energy conversion
device there are substantial technical problems that remain. These
problems are related to cost and endurance. By cost we might take a
figure of $160 per kilowatt of installed powerplant manufacturing
cost; for endurance, 20 years operation. Improvements must be made
with respect to the present materials of construction and electrode
materials such as binders and catalysts. It is obvious that directly
related to the endurance of the fuel cell are the electrolyte and

the corrosion rates and electrode performance that the electrolyte generates.

To improve the relative position of the fuel cell as a power generating device, two main approaches are being taken; one, the improvement of electrode catalysts, the second, the improvement of the electrolyte. These are, of course, interdependent. A specfic catalyst must function and endure in a specific electrolyte.

The present research is concerned with the second approach to the problem, electrolyte improvement, and the selection of new electrolytes with better chemical, physical, and electrochemical properties than those presently used.

II. SCOPE OF THE PRESENT RESEARCH

The properties of the desired fuel cell electrolyte have been described in detail in a previous report from this laboratory (2). Briefly, the following qualifications are required

a) the electrolyte should be a good medium for the oxidation of the fuel

b) the electrolyte should be a good ionic conductor

c) the electrolyte should be a good solvent for active materials and for material transport

d) the electrolyte should be chemically and electrochemically stable over the operating temperature range

e) the electrolyte should possess proper vapor pressure and viscosity characteristics

f) the electrolyte should not be corrosive to fuel cell electrode materials or cell container materials.

Based on these properties a search is underway for chemical compounds, inorganic and organic, that will possess these properties and yet not possess those properties associated with phosphoric acid that have been found to be detrimental to fuel cell operation or endurance.

Thus, the scope of the research includes identifying potential new fuel cell electrolytes and evaluating them with the following chemical or electrochemical tests

    hydrolysis

    thermal stability

    tests for halide ion (for halo-substituted compounds)

    test for decarboxylation (for carboxylic acids)

    solubility

    conductivity

    vapor pressure

    hydrate formation

    wetting of Teflon

    surface tension

    viscosity

    electrochemical stability

    adsorption of H_2 and propane on Pt electrodes

    electrooxidation of H_2 and propane

    electroreduction of air.

III. CHEMICAL AND PHYSICAL PROPERTIES OF POTENTIAL ELECTROLYTES
      AS REPORTED IN THE LITERATURE

The initial survey concentrated on protonic organic acids. The protonic restriction was based on the desirability of finding an

electrolyte suitable for the hydrocarbon-air fuel cell, i.e., a CO_2
rejecting electrolyte. Also H^+ ions are required in the stoichiometry
of the electrode reactions as well as providing solutions with
high conductivity.

The literature search collected data on four classes of compounds

1. carboxylic acids--mono, di and poly, both aliphatic and
   aromatic

2. substituted carboxylic acids, particularly halo substituted
   aliphatic acids.

3. sulfonic acids--mono, di and poly, aliphatic, aromatic
   and bicyclic

4. substituted aliphatic sulfonic acids.

1. Carboxylic Acids

Aliphatic carboxylic acids (3,4,5)

In the saturated mono carboxylic acid the -COOH group is resistant
to reduction. But the β-position of a fatty acid is the primary
point of attack in a reaction. The acid is not oxidized by air
at ordinary temperatures but is by oxygen at elevated temperatures,
especially in the presence of catalysts. $KMnO_4$ can degrade the
carboxylic acid to give quite heterogeneous products. Also biological
oxidative degradation involves the β-position. H_2O_2 attacks the acid,
e.g., a 3% H_2O_2 solution oxidizes butyric acid to β-hydroxy butyric
acid and then to acetoacetic acid and finally to acetone. The -COOH
group is relatively unstable at high temperatures and decarboxylation
is a predominant reaction in the higher temperature range, in the
presence of catalysts yielding ketones. Lower acids yield ketones,

olefines and cyclic hydrocarbons at 600°C; the presence of catalysts greatly lowering the temperature at which the fatty acid undergoes decomposition.

The carboxylate ion of the aliphatic acid is anodically oxidized at the Pt electrode at a very high positive potential, i.e., at +2.3 volts. The mono carboxylic acid has a very low solubility, low conductivity and high pk_a value.

The unsaturated mono carboxylic acid is a reducing agent and is generally not stable.

In view of this stability, aliphatic carboxylic acids, saturated and unsaturated, are not considered as promising electrolytes at this stage.

Di and poly-acids. The first effect of introducing a second carboxyl group is the decrease in the stability of the dicarboxylate anion. Formation of anhydride by loss of water, and decarboxylation usually result. The lower members decarboxylate quickly and the higher members form lactones, or anhydrides. pk_a values are low enough but supporting electrolytes may still be needed. Under a variety of pyrolytic conditions, fatty acids and their derivatives may suffer simultaneous or successive decarboxylation and dehydrogenation to unsaturated hydrocarbons. In a number of instances aromatic hydrocarbons or ketones are formed. Except in the presence of catalysts these are relatively resistant to the action of H_2O_2. When oxidation occurs, it is not specific or directed and a wide variety of products from partial oxidation have been identified such as aldehydes,

hydroxy acids, ketones, hydrocarbons as well as CO_2. In a buffered oxidation system the acid is always oxidized to CO_2.

In view of their instability, we are not considering di or poly carboxylic acids as promising electrolytes.

Aromatic carboxylic acids (3,4,5,6)

These are not strong acids (pk_a values are typically in the range of 4-5 at $25^{\circ}C$. The dicarboxylic acids are sparingly soluble in water. The tricarboxylic, the asymmetric ones, like trimellitic acid have reasonably high acid strengths although the solubility is rather low, i.e., less than 10 grams in 100 ml. With neutralization of one or two of the carboxyl groups a good protonic solvent may result. Trimellitic acid is being given further consideration.

2. Substituted Carboxylic Acids (3-8)

The halogen substituted carboxylic acids fall into two subclasses, those with chlorine, bromine and iodine substitution and those with fluorine substitution. Those with chlorine, bromine, and iodine substitution will be discussed first. These acids are stronger than the corresponding unsubstituted acids. But the kind and position of the halogen atoms in the alkyl chain affect the strength of the acid. A halogen in the α position increases the acidity far more than in the other positions. The effect seems to be electrostatic, the ionizable proton is in a region of relatively high positive charge because it is closer to the positive than the negative end of the larger C-X dipole. The ease of fission of the carbon-bromine bond in the 2-bromo alkanoic acids appears to be related to the length of alkyl chain.

All of these halogen substituted acids are unstable to hydrolysis. With α-halo acids, substitution reactions predominate during hydrolysis; with β-halo acids, unsaturated acids are formed and with γ-acids lactones are formed. These reactions are accelerated by the presence of alkalis. The product, irrespective of the position of the halogen, is formed either by dehydrogenation or by substitution of new groups. This applies to di and poly halogen substitution as well.

In polarographic reduction according to the equation

$$RCH-BrCOOH + H^+ + 2e \longrightarrow RCH_2COOH + Br^-,$$
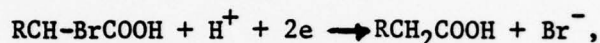
the ease of reduction increases progressively as the homologous series is ascended from acetic to decanoic acid.

The ease of replacement of the halogen in fatty acids is in the same order as in alkyl halides, namely $RI > RBr > RCl > RF$. The bromo and chloro acids can be selectively reduced electrolytically under controlled conditions.

In view of the above reactions no compound was chosen from the chlorine, bromine, or iodine substituted carboxylic acid subclass.

Fluoro-containing carboxylic acids respond normally in many chemical reactions although the reaction rates are determined by the contribution of fluorine to the overall polarity in reactions involving ionic mechanisms. The CF_3 group, for example, is strongly electronegative and exerts a pronounced effect when it is not too remote from the carboxyl group.

Two illustrations are included here to show the unique characteristic bestowed on the carboxyl group by fluoro-substitution.

$$CF_3 - \overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}} - COOH$$
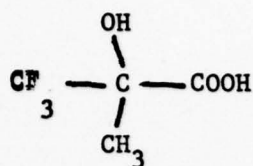
α-trifluoro methyl-α-hydroxy propionic acid

(trifluoro-lactic acid) shows an unusual reluctance to form a lactide whereas the unsubstituted acid dehydrates very easily.

Removal of F from C-F to form an olefin is much more difficult energetically than to remove H_2 from C-H. With partial fluorination the compounds become unstable.

β-fluoro acids resemble β-hydroxy acids in the ease in which unsaturates are formed. In β-difluoro acids this activity should be increased because of the additional inductive effect of the $-CF_2-$ which makes the α-H more mobile.

Difluorosuccinic acid $(CHF-COOH)_2$ is extremely reactive even with water and immediately forms acetylinic dicarboxylic acids.

Some observations on specific members are pertinent in evaluating this subclass of compounds.

Trifluoroacetic acid hydrolyses rather easily.

Trifluoroacetic acid decomposes thermally, very likely, to give a difluorocarbene and CO_2.

Perfluoropropionic acid shows a tendency for hydrolysis.

In water, perfluorobutyric acid, C_3F_7COOH, slowly decarboxylates at 150°C. The aqueous solution of C_3F_7COOH has essentially the same pH as would be calculated for complete dissociation. The F atoms are stable toward hydrolysis. The compound withstands refluxing with dilute base for hours with negligible formation of fluoride ions.

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Decarboxylation reactions are difficult with monocarboxylic acids.
See Table I for some data.

Perfluoroadipic acid. In the presence of $Ba(OH)_2$ decarboxylation
takes place at about $280^{\circ}C$.

One source (8) says that perfluoromalonic acid decarboxylates
readily like malonic acid whereas another source (7) says that
difluoromalonic acid, unlike malonic acid, is stable up to 160°.

The silver salts of mono and dicarboxylic acids react readily
with halogens, Cl_2, Br_2 and F_2, around $80-100^{\circ}$ to give the respective
halides.

The trifluoro methyl group in the β-position is hydrolysed at 100°
in the presence of 2N NaOH, e.g. $CF_3-CH-COOH$ to CH_3CH

$$CH_3 \qquad\qquad (COOH)_2$$

Unsaturated and aromatic perfluoro acids and derivatives are
less stable.

The K and Na salts of perfluoroacids undergo thermal decomposition
as follows:

$$CF_3(CF_2)_3COOK \xrightarrow[10mm]{270^{\circ}} \text{Unsaturated Hydrocarbons.}$$

Free perfluorocarboxylic acids lose HF and CO_2 and form a
perfluoro-olefin when heated to a higher temperature.

Electrolysis of fluorinated alkyl acids in the presence of sodium
methoxide gives fluorinated paraffins by coupling.
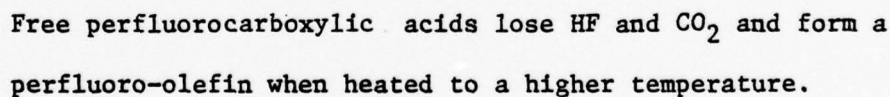
Perfluoroacetic acid is a good catalyst for polymerization and
is a good condensing agent.

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With respect to physical properties the effect of fluorine atoms on the acids is to increase the density, to decrease the refractive index, to lower the surface tension, and to increase the absolute viscosity.

Most of these fluoroacids form hydrates or compounds containing some definite hydrate or water-containing azeotropic mixture. The higher perfluoroacids in aqueous solutions are found to lower the surface tension of water to a larger extent than any other type of compound. The solubilities go down as we ascend the series; there is foaming and gel formations in aqueous solutions. From these observations it may be concluded that if any compound is to be chosen from this subclass the following guidelines should be used.

1. The maximum number of carbon atoms in the mono or dicarboxylic acid should be 4 or 5 and the minimum number 3.

2. The compound should be completely fluorinated and there should be no unsaturation or aromatic rings.

On the basis of the foregoing we have selected perfluorobutyric, C_3F_7COOH, perfluorosuccinic, $(CF_2COOH)_2$ and perfluoroadipic, $(CF_2)_4C_3F_7COOH$, acids for further study.

3. Sulfonic Acids (9, 10)

Aliphatic sulfonic acids

The lower members are strong electrolytes but from heptane upwards show a behavior similar to that observed with solutions of higher soaps, i.e., they form colloidal solutions.

RCH_2SO_3H: Boiling with dilute NaOH solution is without effect but heating in 5% NaOH solution above 300° under pressure results in slow decomposition.

The aliphatic sulfonic acids are, in general, inert towards the action of Cl_2 under ordinary circumstances.

Ethane sulfonic acid is stable towards chlorine but with solid alkalis reacts to give ethylene. The higher members, invariably, exhibit the properties of colloidal electrolytes.

Methionic acid or methanedisulfonic acid, $CH_2(SO_3H)_2$, is a hygroscopic material which is strongly acidic in aqueous solutions. It forms a solid hydrate which separates from a concentrated solution of water. It is very stable to heat, acid, and alkali. No reaction takes place when heated with strong oxidizing agents such as nitric acid or chlorine. See Table I for other properties.

Aromatic sulfonic acids (9-10)

A basic characteristic of this class is ease of hydrolysis. Complete removal of water is essential for stabilization. Even the carboxyl substituted acids share this property. This applies to both compounds with the benzene ring as well as the naphthalene ring. Aromatic sulfonic acids, will be put to more thorough testing procedures before any decision is made.

4. Substituted Aliphatic Sulfonic Acids (9)

Compounds such as the fluorinated substituted aliphatic sulfonic acids, e.g., trifluoromethanesulfonic acid are being considered elsewhere and will not be discussed here.

The α-hydroxy acids undergo a variety of reactions. They decompose both in acid and alkali solutions giving the original carbonyl compounds.

A carboxyl substitution in the hydrocarbon chain increases the stability of the aliphatic sulfonic acid.

e.g. sulfoacetic acid CH_2-COOH
$$|$$
$$SO_3H$$
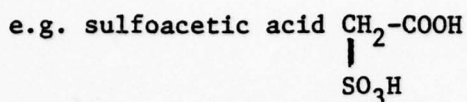
This is a hygroscopic solid which crystallizes as a monohydrate. It is very stable, unlike malonic acid, undergoing no decomposition when boiled with dilute acid or in alkaline solution. By heating to 190°C with conc. H_2SO_4, CO_2 is evolved. With heat alone decomposition sets in at 245°C. Electrolytic oxidation gives CO_2 and H_2SO_4. (This information is from a 1914 paper and it does not give the decomposition potential (21). See Table I for other physical data.

A bicyclic sulfonic acid 10-camphor (dl) acid is very soluble in water, stable and does not decompose readily according to the literature. See Table I for other physical properties of this compound.
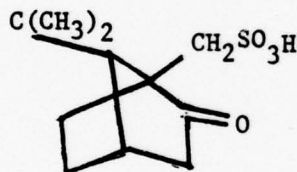
From a consideration of the literature bearing on the properties of the sulfonic acids, substituted and unsubstituted, it was decided that sulfoacetic acid, methionic acid, 1,2,3 propane sulfonic acid, and 10-camphor (dl) sulfonic acid will all be tested for suitability as fuel cell electrolytes.

5. Summary

Some of the pertinent data on those compounds of special interest are collected in table I. (11-14)

Table I. A Summary of The Available Data on Some Proposed Electrolytes.

Compound Name and structure (pk_a, or k_a, where available)[a]	m.p./b.p.(^oC)	Solubility and known reactivity	Specific conductance (ohm^{-1}cm^{-1}, 40^oC) (Measured here)
1. Trimellitic Acid (solid) (3.0×10^{-3} at 25^oC	225-235° with decomposition	5 gms in 100 ml. water at room temperature and increases to 8 gms or so at higher temperatures. An aq solution of potassium dihydrogen salt will be used as the electrolyte.	0.112 for a 10% solution
2. Heptafluorobutyric acid (liquid) C_3F_7 COOH C_3H_7COOH (k_a= 0.68) Relative acidity is the same as HNO_3.	bp 120-121°	Miscible in water; slow decomposition at 150° in the presence of water. Decarboxylation at higher temperatures on heating.	44% solution 0.239.
3. Sulfoacetic Acid $CH_2 - COOH$ $\vert$ SO_3H Very hygroscopic darkly colored solid.	mp of Mono-hydrate 84-86°	Very soluble in water. Very stable to heat. Decomposition starts at 245^oC. With conc H_2SO_4, CO_2 is lost at 190C.	18% solution (as is) 0.3085. 58% solution 0.4640.
4. Methane disulfonic acid (Methionic acid) $CH_2 - SO_3H$ $\diagdown SO_3H$	bp 220°	Very soluble in water very hygroscopic; separates as a monohydrate from concentrated water solutions. Very stable to heat; slight decomposition at 160° C. Very stable to oxidizing agents like HNO_3 or Cl_2.	

Table I. continued

5.	10-Camphor-Sulfonic acid	(dl)	Melts with decomposition at 193°C	Very soluble in water. Can be reduced with Na and alcohol. On fusion with KOH gives campholenic acid	20% solution 0.2115

50% solution 0.293 |

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IV. CHEMICAL AND PHYSICAL PROPERTIES OF POTENTIAL ELECTROLYTES-

EXPERIMENTAL

From the above literature review and other considerations, a number of compounds were selected for further study. These included the *following*:

sulfoacetic acid

trimellitic acid

dl-10 camphorsulfonic acid

methionic acid (methane disulfonic)

perfluorosuccinic or perfluoroadipic acid

1,2,3 - propane trisulfonic acid

heptafluorobutyric acid

These compounds were subjected to the following types of test:

specific conductance

wetting (contact angle on Teflon)

chemical stability

vapor pressure of solutions

electrochemical behavior (voltage sweep)

Specific conductance

The conductances of a number of solutions are given in table II; included is the conductance of phosphoric acid. In Table III, the conductances of solutions of trifluoromethane sulfonic acid monohydrate (TFMSA·MH) are given for comparison. These latter data at 40° and 80°C are plotted in figure 1. It is apparent that, with the exception of the chloroacetic acids, these solutions possess sufficient conductivity to make them interesting electrolytes.

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Table II. Conductance Data for Solutions of Proposed Electrolytes

Compound	Concentration (weight percent)	Temperature	Specific conductivity (ohms^{-1} cm^{-1})
H_3PO_4	85%	40°C	0.1381
Dichloroacetic acid	80% vol.	40°C	0.01883
Trichloroacetic acid	80 wt. %	40°C	0.01856
Benzene Sulfonic acid	5%	40°C	0.1217
Sulfosalicylic acid	5%	40°C	0.0767
Sulfoacetic acid	18%	40°C	0.3089
	58	39.8	0.4640
Heptafluorobutyric acid	43.59	40°C	0.2388
Trimellitic acid monopotassium salt	10	40°C	0.1124
dl-10 camphorsulfonic acid	20.81 (49.3 gm/100ml)	40°C 40°C	0.2149 0.2920

Table III.   Conductivity of Water solutions of Trifluoromethane
            Sulfonic Acid Monohydrate Solutions

Concentration (weight percent)	40°C	specific conductance (ohms^{-1}cm^{-1}) 80°C
100	0.01122	0.0305
90	0.07109	0.1302
80	0.1847	0.3089
70	0.3232	0.5122
60	0.4309	0.7687
50	0.5500	0.8082
40	0.5750	0.8109
30	0.5400	0.7774
20	0.3802	0.5578
10	0.2391	0.3161
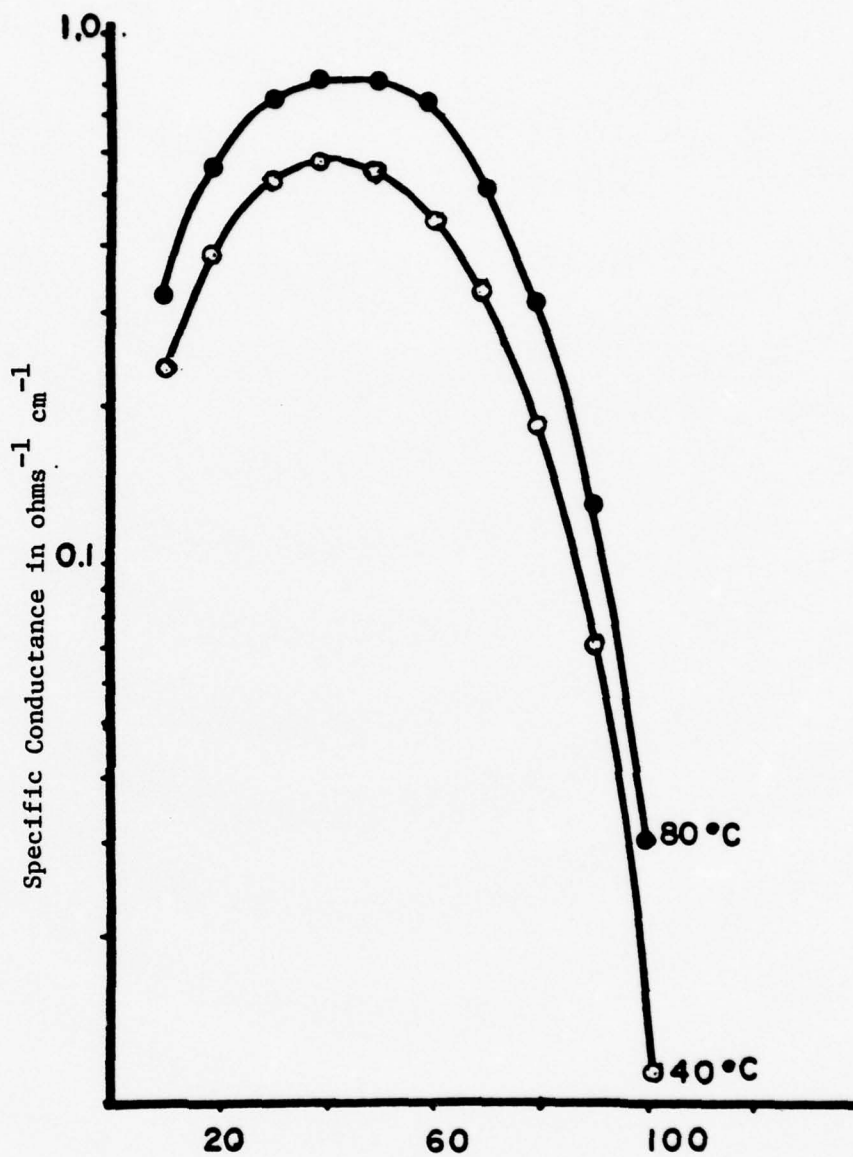
Weight percent concentration of aqueous TFMSA-MH.

Figure 1. Specific conductance of aqueous solutions of trifluoromethanesulfonic acid at 40° and 80°C.

Wetting (contact angle on Teflon)

The contact angle on Teflon was measured with a procedure described in a previous report (15). The results are given in Table IV. Those solutions with a contact angle of greater than 90° are considered to be non-wetting to Teflon.

Chemical Stability

The aqueous solutions of the acids were tested qualitatively for decomposition products. They were then refluxed and, while refluxing, argon gas was passed through the solution. The argon passed then through a train consisting of silica gel to pick up water and pre-treated barium hydroxide to pick up CO_2, SO_2, or HF. The changes in weight in the absorption tubes were determined. The acidities of the solutions, before and after refluxing, were determined volumetrically. The results of certain preliminary tests are given in table V and the results of some quantitative hydrolysis tests in Table VI. Solutions of sulfoacetic acid and dl-10 camphor sulfonic acid appear to be chemically stable to hydrolysis. On the other hand the aromatic sulfonic acids appear to be very susceptible to hydrolysis. This reaction must be confirmed because it could lead to the discarding of a whole class of electrolytes. The set up for the stability testing is shown in figure 2.

Vapor pressure of solutions

The vapor pressures of selected electrolyte solutions were measured by the isopiestic method (16-18). The method consists of equilibrating solutions of known and unknown vapor pressures in an isolated chamber for an extended period of time, during which period a good thermal contact is established between the pair. After equilibration the vapor pressures of the two solutions are the same and the respective concentrations
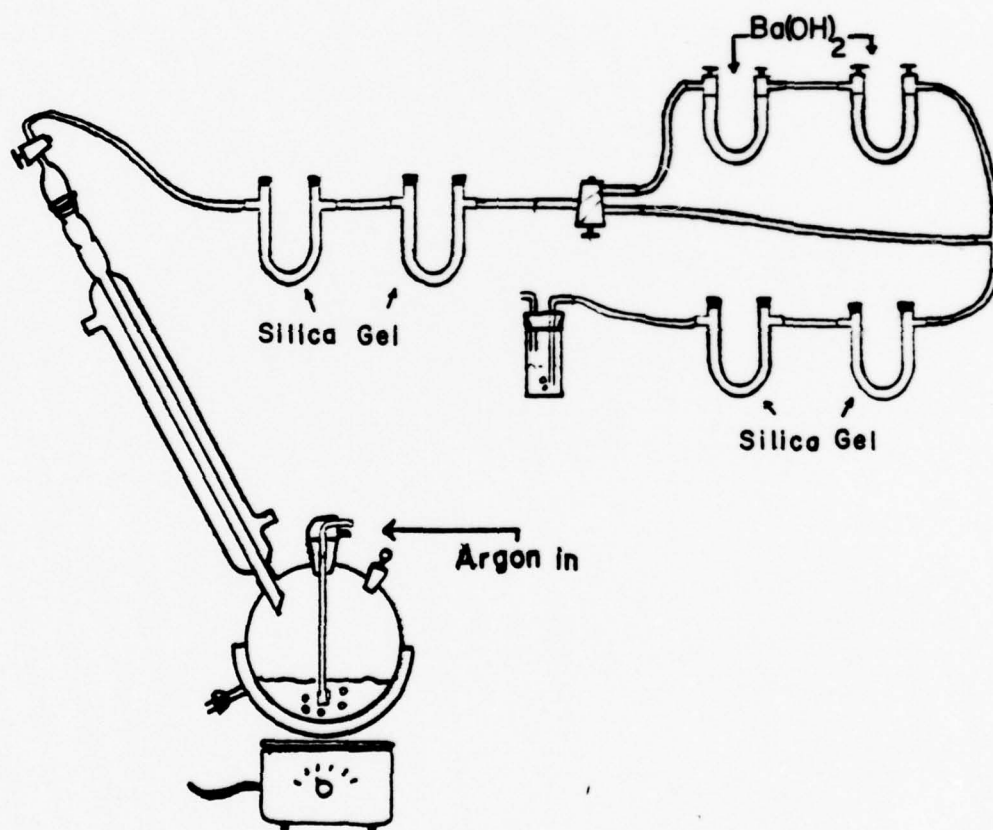
- 19 -

Figure 2. Set up for the Stability Testing

are measured. A chamber to permit such a thermal contact between two pairs of pyrex containers with a provision to close and open the individual containers without opening the chamber was designed and fabricated. This chamber is schematically shown in figure 3. The chamber was set inside a thermostated air oven during the experiment which lasted from 24 hours to a week. One of the drawbacks to the method is that the concentrations of the solutions cannot be prechosen, i.e., at a specific temperature the concentration of the unknown solution is adjusted so that the vapor pressure of this unknown solution is equal to the vapor pressure of the reference solution. Thus, the method requires knowing accurately the vapor pressure of a reference solution. In this investigation phosphoric acid solutions were used as references as the vapor pressure data over a wide range of temperatures are available. These data are compiled in a vapor pressure-composition plot in figure 4 which gives a series of isotherms. In figure 5 the vapor pressure is plotted versus the inverse temperature. The data for the unknown solutions were interpreted with these curves.

Table VII presents some electrolytes at concentrations isopiestic with approximately 85% phosphoric acid at room temperature.

Electrochemical behavior (voltage sweep experiments)

The experimental set up and the electrochemical cell were similar to that previously described (15). The following changes were made in these studies.

(1) A saturator was introduced into the argon bubbling system to compensate for water loss in aqueous solutions whenever they were used as electrolytes.

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Table IV.   Contact Angles of Electrolytes on Teflon at

Room Temperature. (26° ± 1°C)

Solution	Concentration weight percent	Contact angle on Teflon
TFMSA · monohydrate	100	72.83°
Methane sulfonic acid	100	93.59°
Trimellitic acid monopotassium salt	10	97.59°
d1-10 Camphor sulfonic acid	50	81.06°
Sulfoacetic acid	59	90.15°

Table V. Summary of Preliminary Tests on Electrolytes

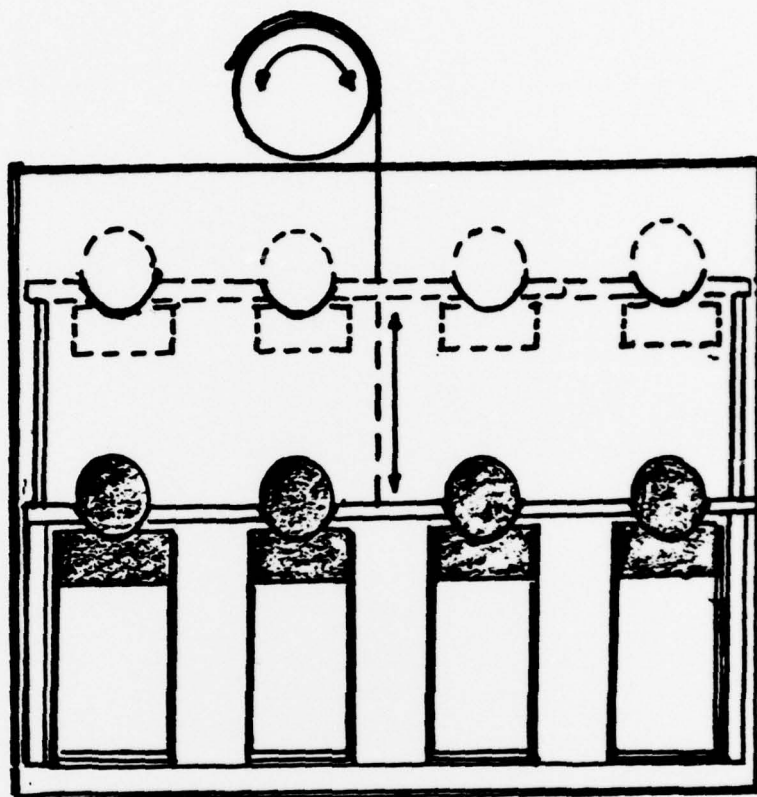| Acid	Nature of test	Remarks
Dichloroacetic acid	Hydrolysis test	Very unstable in the presence of water.
Trichloroacetic acid	"	"
Dibromosuccinic acid	"	"
Heptafluorobutyric acid	Vapor pressure (see Table VII)	Very volatile.
Perfluorooctanoic acid	Solubility	Very soapy solution (froths and foams)
2-3 naphthalene dicarboxylic acid	Solubility	Very low solubility.
Trimellitic acid	Solubility	Sparingly soluble and hence a monopotassium acid salt will be tested.
5, Sulfosalicylic acid	An aqueous solution was tested with solution $BaCl_2$	All the aromatic sulfonic acids give a precipitate on standing at room temperature and more easily on heating.
1,5 naphthalene disulfonic acid	"	"
1,3,6 naphthalene trisulfonic acid	"	"
Benzene sulfonic acid	"	"
Meta carboxylic benzene sulfonic acid	"	"

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Figure 3. A schematic of the isopiestic vapor
pressure cell.

Table VI.   Results of Quantitative Hydrolysis Testing

Acid Solution	Volumetric Analysis Strength		Increase in Weight of Ba(OH)$_2$ Tubes
	Before	After*	
Sulfoacetic acid (approximately $\approx$ 59 gms in 100 ml)	0.368N	0.372N	2.96 mgs. (a)** 17 mgs. (b)
Trifluoro-methane sulfonic acid monohydrate ($\approx$ 42 gms in 100 ml)	0.2133N	0.2096N	18.7 mg (a) 13.5 mg (b)
10-dl Camphor sulfonic acid ($\approx$ 50 g in 100 g)	0.1041	0.1062	30.5 mg (a) 26.8 mg (b)

* Water loss was compensated before estimation. Since the volume compensation was approximate these solutions may be considered as stable to hydrolysis.

** (a) indicates initial experiment, (b) a similar experiment conducted 24 hours later.

Table VII. Concentrations of Some Electrolytes, Isopiestic With About 85% H_3PO_4 at Room Temperature

Electrolyte	Initial Concentration (weight percent)	Final Concentration			
		(1) t=24.5°C ± 0.5	(2) 25.5°C ±0.5	(3) 26.5°C ±0.5	(4) 26.5°C ±0.5
Phosphoric acid	85	79.6 (5.5mm)*	82.28 (4.5)	83.10 (4.5)	80.17 (5.35)
TFMSA-Monohydrate	100	--	91.98	95.43	86.71
Perfluoro butyric acid**	100	weight loss 4.44	4.53	4.67	--
Methane disulfonic acid	50	52.05	51.30	51.10	54.25
10-Camphor (dl) sulfonic acid	50.6	56.62	55.82	54.67	67.26
Ethane 1-2 disulfonic acid	50.85	52.73	--	52.91	58.28
Perfluoro succinic acid	50	50.03	53.64	53.36	62.27
Octafluoro adipic acid	50	57.57	55.31	54.30	63.84***

* values of vapor pressure in mm of Hg given in parenthesis under concentration of H_3PO_4. From references (19,20)

** very volatile liquid

*** this may be the limit of solubility at this temperature.
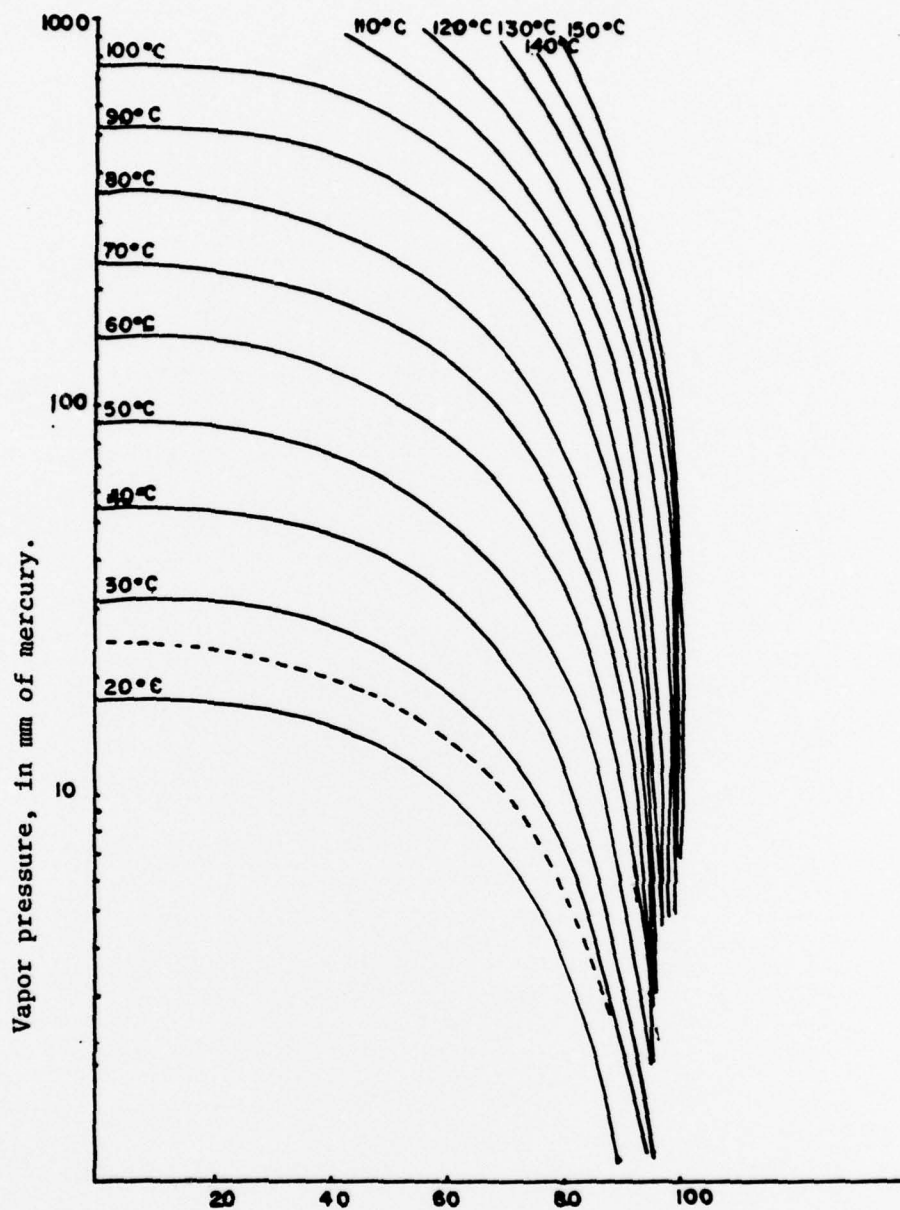
Weight percent concentration of aqueous phosphoric acid solutions.

Figure 4. Vapor pressure isotherms of phosphoric acid solutions plotted from the data given in references 19 and 20.
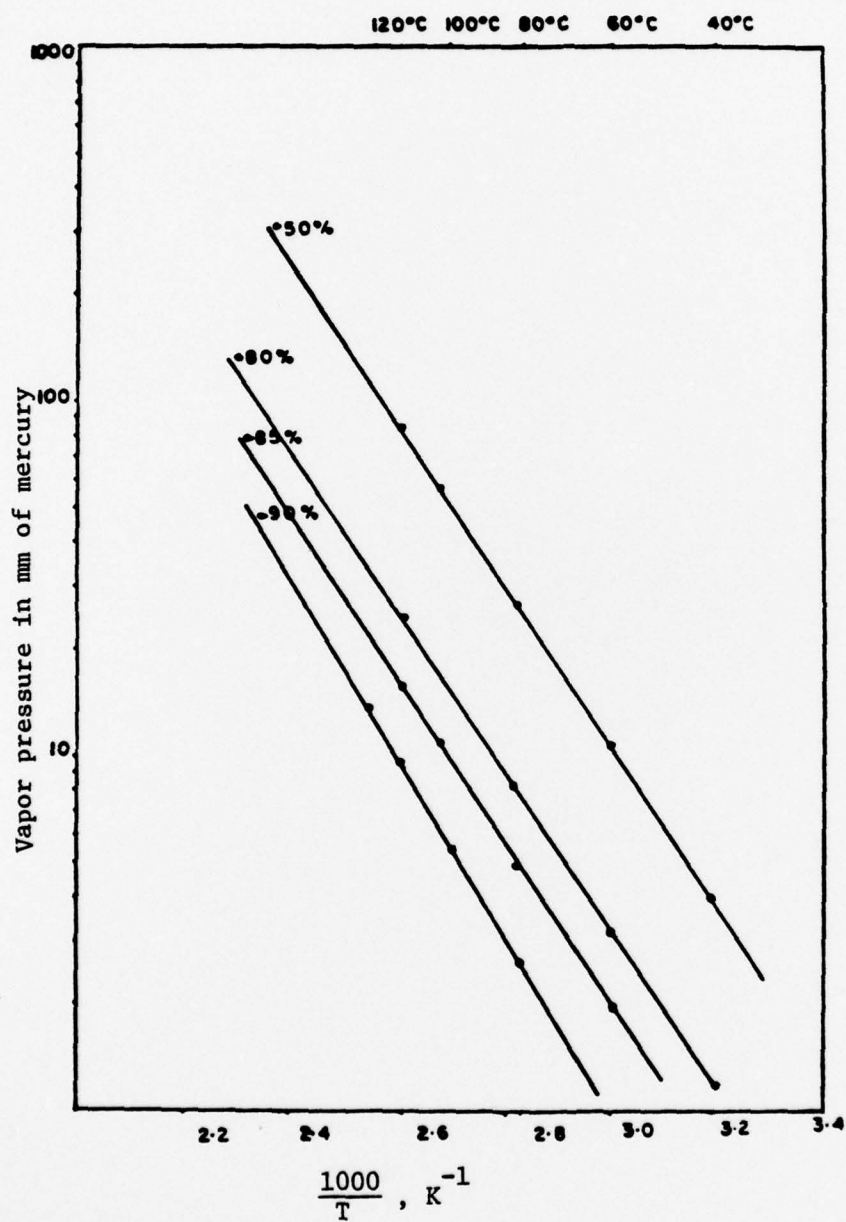
Figure 5.   Vapor pressure plots of phosphoric acid solutions
versus inverse temperature data from references 19 and 20.

(2) A lower temperature was used for the preliminary work reported here.

(3) Purging with argon was continued for a longer period of time before the start of the scan, but was stopped during the voltage scan to leave the system undisturbed.

(4) A new platinum electrode was used.

(5) The rate of sweep was reduced and a shorter voltage range was used.

The cyclic scan for dichloroacetic acid is given in figure 6. The solution was a 50% by volume solution with H_2O. The rest potential was 310 mV (versus DHE) and the scan rate was 50mV/sec.

Sweeping in the anodic direction a very low current was observed until about 600mV, then the current began to increase in the negative direction. The current changed from 0 μA to -20 μA between the anodic potentials 600 mV and 1200 mV. The scan direction was reversed at 1500 mV. Then the current decreased steadily from -40 μA to -6 μA as the potential decreased by 500 mV. A slight increase in current occurred and a cathodic reduction peak was found at 375 mV with a maximum current of 8 μA. This peak is likely due to platinum oxide reduction. The dichloroacetic acid used in this experiment was vacuum distilled at 6mm from Fisher Scientific, purified grade. This electrolyte and other halogenated acids were found to be easily hydrolyzed in aqueous solution.

The voltage scan obtained with a solution 31% by weight of dl-10 camphor sulfonic acid is given in figure 7. This run was made at $80^{o}C$ at a scan rate of 10 mV/sec. The rest potential was 360 mV. Preliminary to these experiments the system was purged for two hours with argon.

Figure 6. Cyclic voltammogram of dichloroacetic acid.
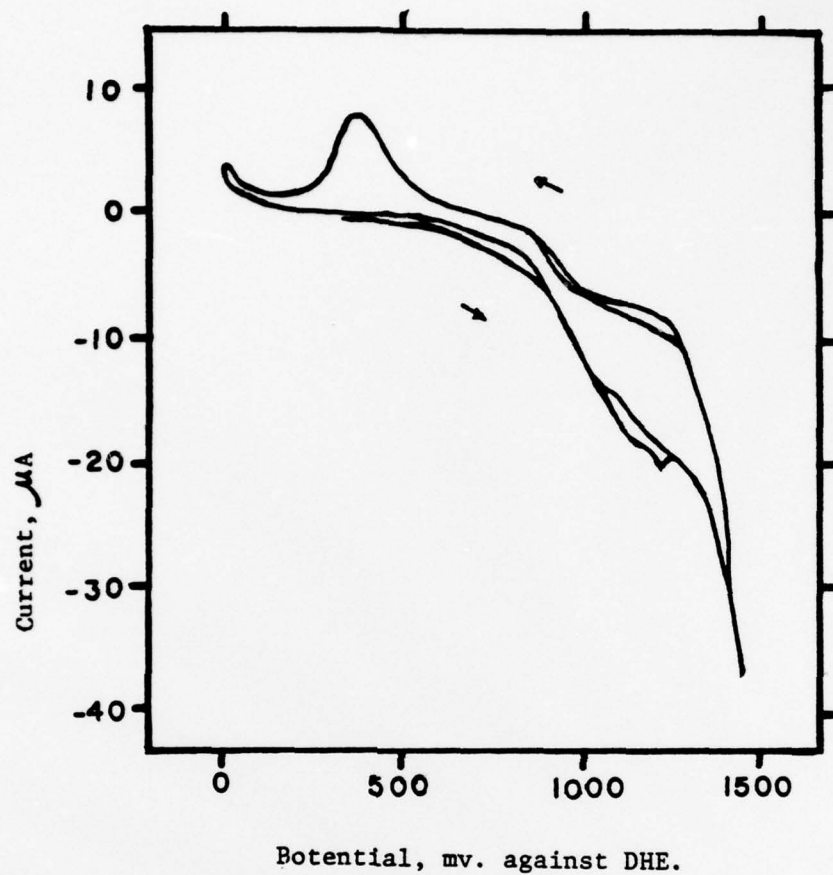
Dichloroacetic acid

Concentration	50% Volume
Bubbler	Yes
Temperature	80°C
Rest potential	310 mV (Pt. vs. DHE)
Scan rate	50mV/sec
Voltage range	0 to 1.5 V
Quiescent solution	No

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Figure 7. Cyclic voltammogram of dl-10 camphorsulfonic acid
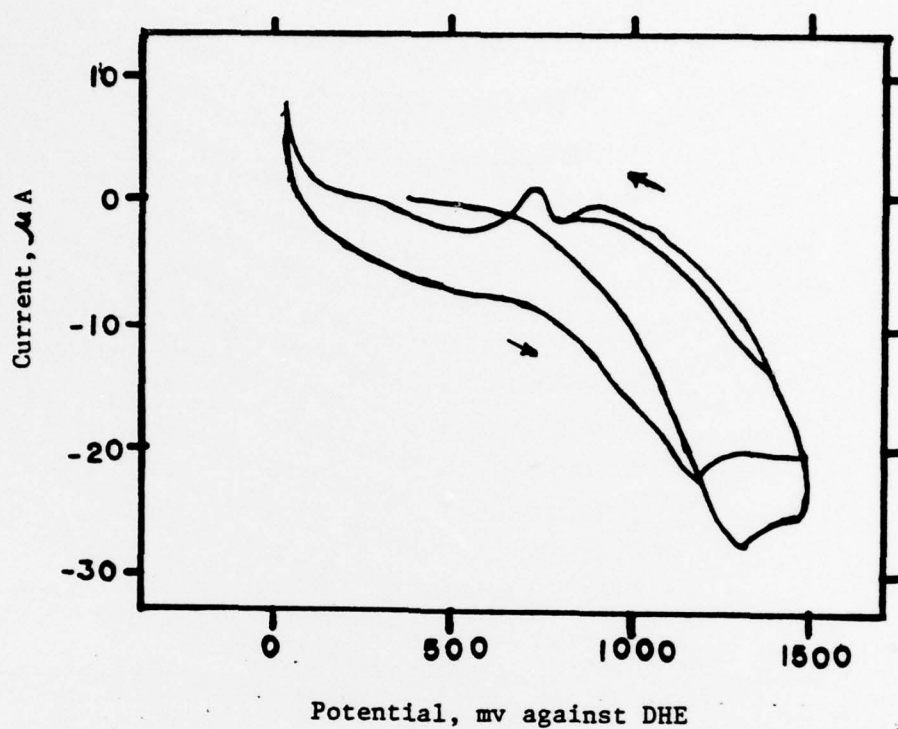
dl-10 Camphorsulfonic acid

Concentration	31% weight
Bubbler	Yes
Temperature	$80^{\circ}C$
Rest potential	360 mV (Pt. vs. DHE)
Scan rate	10mV/sec
Voltage range	0 to 1.5 V
Quiescent solution	Yes

Figure 8. Cyclic voltammogram of heptafluorobutyric acid.

Heptafluorobutyric acid

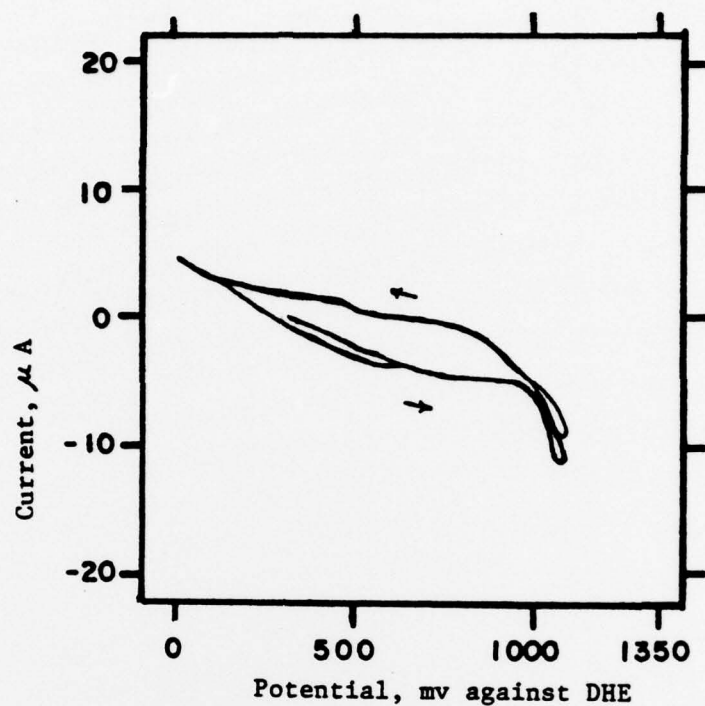|	
Concentration	50% weight
Bubbler	No
Temperature	$80^{o}C$
Rest Potential	300 mV (Pt. vs. DHE)
Scan rate	50mV/sec
Voltage range	0 to 1000mV
Quiescent solution	No

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Hydrogen was then used to purge the system for twenty minutes because of an unusually high rest potential (due to the presence of oxygen). Argon was used a second time to purge the system of hydrogen. Scanning in the positive direction the current increased steadily from 0 μA to -22 μA at which point the anodic potential was 1200 mV. The current then decreased slightly to -18 μA and the scan was reversed at 1500 mV. (The first scan gave a slightly higher current, -27 μA at 1300 mV.) The current increased to 1 μA where a cathodic reduction peak was observed at a potential of 725 mV. The current then dropped off to -2 μA and was nearly steady until zero potential was reached, where the current increase was due to hydrogen reduction. The reduction of current with successive sweeps indicated that some electroactive species were being removed.

The scan obtained with a 50% solution of heptafluorobutyric acid is given in figure 8. Scanning in the positive direction the current increased slightly from 0 μA at a rest potential of 300 mV to about -5 μA at 1000 mV; at this point the current increase was much sharper to a maximum of -11 μA at 1075 mV. The scan was reversed at this point. The current decreased in a regular fashion until a maximum of 5 μA was reached at approximate zero potential. This electrolyte appears to be reasonably stable electrochemically but its vapor pressure appears to be too high.

V. CONCLUSIONS AND DIRECTION OF FUTURE WORK

It appears possible at this point to eliminate certain classes from the list of potential electrolytes. These include aliphatic carboxylic acids and those carboxylic acids that are substituted with

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chlorine and bromine. If the general property of aromatic sulfonic acids, if hydrolyzing in aqueous solution, is confirmed then this class will be eliminated.

Some fluorinated aliphatic acids such as hepta fluorinated butyric acid have several very desirable physical properties such as high specific conductance but their vapor pressures may be too high or at least the perfluorinated butyric acid vapor pressure is too high and it would be necessary to go to a C5 or C6 acid.

Certain sulfonic acids appear of interest such as sulfoacetic acid and 10-dl camphor sulfonic acid. The electrochemical stability of the latter is in question but a more pure material must be obtained for evaluation.

The tricarboxy acid, trimellitic, when used as the mono or di potassium salt appears to possess sufficient solubility and conductivity.

It is planned to study these compounds in more depth particularly in connection with the electrochemical properties referred to above. Then tests would include the employment of the compound in fuel cell type reactions.

The vapor pressure measurement is of critical importance in categorizing these electrolytes. Because of the limitations of the isopiestic method it is intended to go to a direct method for future measurements.

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